

EFFECT OF VARIOUS CATIONS ON THE INITIAL RATE OF FORMATION OF PEROXODISULPHATES

Jan BALEJ and Martin KADEŘÁVEK

*Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received April 11th, 1979

Preparation of peroxodisulphates by electrolysis of mixed solutions of sulphuric acid and various sulphates was studied at low degree of conversion; the partial polarization curves of peroxodisulphate formation and of oxygen evolution obtained from the overall anodic polarization curves and current yields of the principal anodic processes were examined. The mechanism of the effect of various cations on the rate of anodic formation of peroxodisulphates is discussed.

Since the first electrochemical preparations of peroxodisulphate ions as intermediate products of electrochemical production of hydrogen peroxide it has been known¹⁻³ that the overall current yields depend considerably on the kind and amount of cations present in the electrolyzed solution. In the early paper by Elbs and Schönherr⁴ this effect has only been stated, the highest increase in the yield having been observed for Al^{3+} , followed by K^+ , NH_4^+ , etc. The authors admitted, however, that the effect of Al^{3+} could be influenced by the Cl^- ions present in the aluminium sulphate used. Müller and Schellhaas⁵, working with supposedly highly pure chemicals, found approximately the same effect of Al^{3+} , K^+ , and NH_4^+ ions for the current density $j_a = 0.5 \text{ A cm}^{-2}$; the effect of other cations (H^+ , Na^+) was appreciably lower, in accordance with the findings of Elbs and Schönherr⁴. The measurements of Essin and Alfimova⁶ indicate the order of efficiency roughly $\text{NH}_4^+ \approx \text{K}^+ > \text{Na}^+ \approx \text{Al}^{3+}$, whereas according to Matsuda⁷, the efficiency of the cations investigated by him decreases in the order $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{H}^+ > \text{Mg}^{2+} > \text{Li}^+ > \text{Al}^{3+} > \text{Cd}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+}$, practically independently of the total current density in the region $j_a = 0.1-1.6 \text{ A cm}^{-2}$ in solution of the total composition $\sum c_{\text{SO}_4^{2-}} = 3.5 \text{ mol dm}^{-3}$. Izgaryshev and Petrova⁸ obtained the order of efficiency $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{H}^+ > \text{Mg}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Al}^{3+} > \text{Zn}^{2+}$, although the quantitative effects of the various ions in different experimental conditions were somewhat different. Recently the effect of cations on the kinetics and mechanism of formation of peroxodisulphates has been studied by Chu Yung-chao^{9,10}, particularly for electrolysis of $\text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$ mixed solutions with different molar ratios. The latest results published are those of Smit and Hoogland¹¹, according to which the sequence of univalent cation efficiency is $\text{Cs}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ \approx \text{H}^+ > \text{Li}^+$.

The hitherto published results concerning the effect of various cations are thus mutually rather different, and moreover, they do not cover sufficiently the theoretically as well as technically interesting range of reaction conditions; also, the explanation of the effects is not uniform. Earlier works⁵⁻⁷ ascribed the effect of various cations to an unspecified catalytic effect on the course of the anodic and chemical processes in-

volved. Izgaryshev and Petrova⁸ pointed to a possible relation between the effect of the cation on the current yields of peroxodisulphates and its hydration energy, although the interpretation suggested is correct enough. More recent works⁹⁻¹¹ use rather the concept of specific adsorption of the cations on the oxidized surface of the platinum electrode at high anodic potentials; this concept has also been employed to explain the effect of cations on the oxygen evolution rate¹²⁻¹⁶ (which in fact is a process occurring simultaneously during the anodic formation of peroxodisulphates) as well as on other electrode processes at high anodic potentials¹⁷. In order to make this problem clearer we carried out some measurements which are the subject of the present paper.

EXPERIMENTAL

Apparatus and working procedure: The effect of cations on the initial rate of formation of peroxodisulphates was investigated by means of the same apparatus as used in our previous work¹⁸, the measurement principle being the same too. The stationary anodic polarization curves in the potential region of formation of peroxodisulphates were determined by the potentiostatic method using a potentiostat Wenking ST 72; in order to maintain a low degree of conversion of sulphate to peroxodisulphate ions, the solution electrolyzed was replaced by a fresh one without interrupting the polarization. The rate of the simultaneous oxygen evolution on the platinum electrode was measured and the current yields of oxygen and of peroxodisulphates were calculated under the simplifying assumption that the rate of formation of ozone in the experimental conditions applied was negligible¹⁹. The low degree of conversion maintained warranted the assumption that all peroxy compounds present in the solution were peroxodisulphates. The anodic potential was corrected for the IR drop between the electrode surface and the orifice of the Luggin capillary, determined by the interruption technique by means of an oscilloscope²⁰. The current densities refer to the actual surface of the smooth platinum anode, whose roughness factor was on average 1.5 ± 0.07 . This enabled the overall polarization curves to be resolved into the partial polarization curves of oxygen evolution and peroxodisulphate formation, which form a basis of the subsequent evaluation of the effect of the cations examined on the two principal anodic processes.

In most cases, this effect was investigated by electrolyzing mixed solutions of the total concentration $5M-H_2SO_4 + 1M-M_xSO_4$ (M is the cation), provided that the sulphate was sufficiently soluble; K_2SO_4 and Rb_2SO_4 were added in 0.8M concentration, low soluble sulphates in 0.1M concentration, and in the case of $HgSO_4$ and Hg_2SO_4 as low additions of the sulphates as 0.01M were used. In this manner, the effect of H^+ , Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Cd^{2+} , Zn^{2+} , Hg^{2+} , Hg_2^{2+} , Al^{3+} , and La^{3+} ions was examined. The measurement temperature was 25°C.

The solutions to be measured were prepared from sulphuric acid reagent grade purity, distilled water, and from the sulphates of interest, reagent grade purity, which had been either recrystallized or evaporated with sulphuric acid to remove traces of chlorides, which could distort the effect of the cations.

RESULTS

The overall polarization curves and the partial polarization curves for the formation of peroxodisulphates ($S_2O_8^{2-} - HSO_5^-$) for some of the systems measured, $5M-H_2SO_4 -$

$-1M-M_xSO_4$, are shown in Fig. 1. The curves confirm the finding that a transition region appears on the overall polarization curves at potentials above 2.2 V (R.H.E.) where the Tafel's relation cannot be applied. The partial polarization curves of oxygen evolution (not shown in Fig. 1) have a similar course. In contrast to this, the partial polarization curves of formation of peroxodisulphates obey the Tafel's relation also in this transition region up to the potential of approximately 3 V; in the region of higher potentials, departures from this relation occur in this case too.

The lowest curves (1 and 1', resp.) in Fig. 1 refer to sulphuric acid alone; they practically coincide with those obtained with solutions containing Cd^{2+} or Zn^{2+} ions. Partial substitution of H^+ ions by univalent alkali metal and ammonium cations results in increase of the anodic potentials in the examined region of current densities, but no unambiguous relation between this increase and the characteristic properties of cations could be traced. Also, different ions were found to exert the maximum effect on the shift of the overall polarization curve in different current density regions.

Fig. 2 demonstrates the dependence of the current yields of peroxodisulphates, measured at the quasi-steady state of the electrode¹⁸, on the overall anodic current

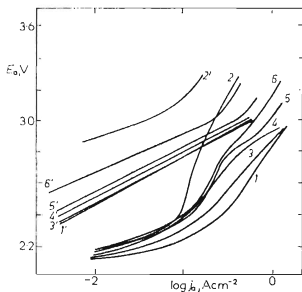


FIG. 1

Overall Anodic Polarization Curves (1-6) and Partial Polarization Curves (1'-6') of Formation of Peroxodisulphates for Electrolysis of Solutions of $5M-H_2SO_4-1M-M_xSO_4$ at $25^\circ C$

Cation $M = H^+$ (1, 1'), Li^+ (2, 2'), NH_4^+ (3, 3'), K^+ (4, 4'), Rb^+ (5, 5'), Cs^+ (6, 6').

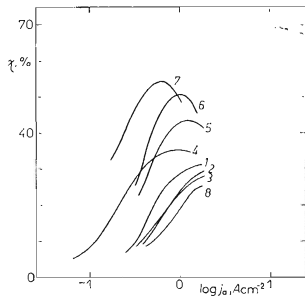


FIG. 2

Dependence of the Initial Current Yields of Peroxodisulphates on the Current Density for Electrolysis of Solutions of $5M-H_2SO_4-1M-M_xSO_4$ at $25^\circ C$

Cation M : 1 H^+ , 2 Li^+ , 3 Na^+ , 4 NH_4^+ , 5 K^+ , 6 Rb^+ , 7 Cs^+ , 8 Cd^{2+} , Zn^{2+} .

density for the same solutions as in Fig. 1. Obviously, the dependences are alike; a maximum appears either distinctly in the current density region measured, or it can be supposed to occur at slightly higher densities than as could be measured with the apparatus employed. As regards the maximum current yields attained, the order of efficiency of cations is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{NH}_4^+\text{H}^+ \geq \text{Li} \geq \text{Na} < \text{Cd} = \text{Zn}$ was found. It was further shown that the current density at which the maximum yield is achieved was found to be the lower, the more efficient is the cation, *i.e.* the higher is the maximum current yield.

The effect of higher relative concentrations of cations on the current yields of peroxodisulphates was measured on the system involving ammonium ions, where the

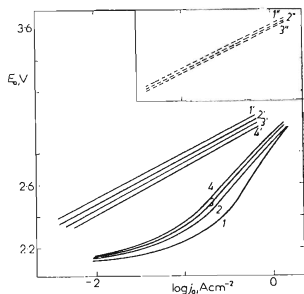


FIG. 3

Overall Anodic Polarization Curves (1-4) and Partial Polarization Curves of Formation of Peroxodisulphates (1'-4') for Electrolysis of Solutions of Total Concentration 6 mol dm^{-3} and with Variable Concentration of $(\text{NH}_4)_2\text{SO}_4$

Concentration of $(\text{NH}_4)_2\text{SO}_4$, mol dm^{-3} : 1, 1' 0, 2, 2' 1, 3, 3' 2, 4, 4' 3. Right top: theoretical shift of the polarization curves of formation of peroxodisulphates due only to the change of equilibrium potential of the anode resulting from the change of concentration of ammonium sulphate; concentration of $(\text{NH}_4)_2\text{SO}_4$, mol dm^{-3} : 1" 1, 2" 2, 3" 3.

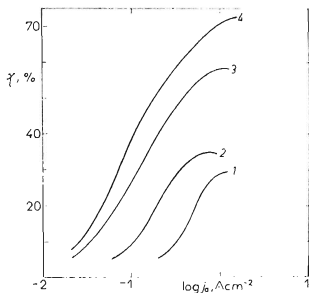


FIG. 4

Dependence of Initial Current Yields of Peroxodisulphates on the Current Density for Electrolysis of Solutions of $\text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$, Total Concentration $6 \text{ mol} \cdot \text{dm}^{-3}$

Concentration of $(\text{NH}_4)_2\text{SO}_4$, mol dm^{-3} : 1 0, 2 1, 3 2, 4 3.

solubility of both the sulphate and the peroxodisulphate is high enough²¹ and which is also the most important from the technical point of view¹⁻³. The total concentration was 6 mol dm^{-3} , the sulphuric acid-to-ammonium sulphate molar ratios were $P_0 = 5, 2, \text{ or } 1$. Solutions with lower P_0 values were not examined, because in technical continuous processes only solutions with $P_0 > 1.0$ are applied¹⁻³.

The overall anodic polarization curves and the partial polarization curves for the formation of peroxodisulphates are shown for these solutions in Fig. 3, the dependence of current yields of peroxodisulphates on the current density is depicted in Fig. 4. It can be seen that the increase of current yields of peroxodisulphates with the increasing relative content of ammonium ions (*i.e.*, with decreasing P_0 ratios), which has been known to occur, is due to the increase in the oxygen overpotential as well as to the speeding up formation of the peroxodisulphate ions. This is associated with the fact that with the increasing content of ammonium ions, the partial anodic polarization curve of oxygen evolution shifts towards higher potentials, while the polarization curves of formation of peroxodisulphate ions are shifted in the opposite direction. In this sense, our results confirm those obtained by Chu Yung-chao¹⁰ for the electrolysis of solutions with the total concentration of the sulphate ions $c_{\text{H}_2\text{SO}_4} + c_{(\text{NH}_4)_2\text{SO}_4} = 4 \text{ mol dm}^{-3}$.

From the point of view of the effect of cations on the shift of the polarization curves, the behaviour of lithium ions is of interest; they bring about a shift in the positive direction of the polarization curves of both oxygen evolution and peroxodisulphate formation (Fig. 1), so that the current yields of peroxodisulphates even at considerably more positive potentials are lower than in solution of pure sulphuric acid (Fig. 2).

The results obtained with lower soluble sulphates are represented in Table I by the maximum peroxodisulphate current yields attained; for cation concentration 0.1 mol l^{-1} , the current density corresponding to the maximum yields was approximately 2 A cm^{-2} in all cases. Results for solutions of $5\text{M-H}_2\text{SO}_4 + 1\text{M-M}_x\text{SO}_4$ are given for a comparison too. The effect of positively acting cations is seen to lower with their decreasing concentration. It was interesting to find that at the concentration $0.1 \text{ mol} \cdot \text{dm}^{-3}$, the second highest activity – after Cs^+ – was exhibited by La^{3+} ions. On the other hand, no positive effect could be traced for Al^{3+} ions, which indicates the incorrectness of the early data^{4,5} and confirms the more recent findings^{7,8} that this effect exerts no or a negative effect.

DISCUSSION

The results of our measurements first of all supply complementary data concerning the effect of the cations in question on the initial current yields of peroxodisulphates over the entire technically interesting current density region $j_a = 0.1 - 2.0 \text{ A cm}^{-2}$ and for sufficiently concentrated solutions of sulphuric acid and the corresponding

sulphates. Smit and Hoogland¹¹ have examined the effect only at $j_a = 1.0 \text{ A cm}^{-2}$, Izgaryshev and Petrova⁸, in contrast, applied technically too high current densities, $j_a = 2-6 \text{ A cm}^{-2}$. Moreover, the quantitative results obtained by different authors in comparable conditions are rather different^{4,7}.

The effect of positively acting cations at a given temperature and total solution composition was found to depend also on the overall current density j_a or the anodic potential E_a , which was not clearly apparent from the earlier works. For this reason, no unique order of efficiency of the cations can be given. At the same time, the fact that the current yields of peroxodisulphates grow with increasing relative content of the positively operating cations^{4,7} has been confirmed.

The results as a total can be used for discussion of the current views upon the cause of the cation effect as observed. These views can be divided into three groups as follows: a) the cations exert an unspecified catalytic effect⁵⁻⁷; b) the different hydration of the cations affects the degree of hydration of the sulphate anions and thereby also the rate of their discharge to the peroxodisulphate ions⁸; c) the different adsorption of the cations on the oxidized surface of the platinum anode affects the rate of discharge of the sulphate ions from the outer Helmholtz layer with the forma-

TABLE I

Maximum Current Yields of Peroxodisulphates $\chi_{\text{S}_2\text{O}_8^{2-}}$ and the Corresponding Current Densities $j_{a,\text{max}}$ for Electrolysis of Mixed Solutions of $5\text{M-H}_2\text{SO}_4 + 1\text{M-M}_x\text{SO}_4$ (solution I) and $5\text{M-H}_2\text{SO}_4 + 0.1\text{M-M}_x\text{SO}_4$ (solution II) at 25°C

Cation	Solution I $\chi(\text{S}_2\text{O}_8^{2-})$ %	$j_{a,\text{max}}$ A cm^{-2}	Solution II ^a $\chi(\text{S}_2\text{O}_8^{2-})$ %
H ⁺	30	1.6	28
Li ⁺	30	2.0	28
Na ⁺	27-30	2.0	25
NH ₄ ⁺	37	1.0	30
K ⁺	45 ^b	1.25	30
Rb ⁺	51 ^b	1.0	33
Cs ⁺	55	0.6	36
Cd ²⁺	25	2.0	25
Zn ²⁺	25	2.0	25
Hg ²⁺	—	—	20 ^c
Al ³⁺	—	—	25
La ³⁺	—	—	35

^a At $j_{a,\text{max}} = 2 \text{ A cm}^{-2}$; ^b $5\text{M-H}_2\text{SO}_4 + 0.8\text{M-M}_x\text{SO}_4$; ^c $5\text{M-H}_2\text{SO}_4 + 0.01\text{M-HgSO}_4$.

tion of peroxodisulphates^{10,11}. Although the various explanations rely on apparently quite dissimilar phenomena and the previous authors considered always only one of them, we consider them to have a common basis, which can be deduced from the present-state knowledge of the properties and behaviour of the interface between the Pt anode and the concentrated mixed aqueous solutions of sulphuric acid and the various sulphates at high anodic potentials.

First of all, we must bear in mind that two principal independent processes occur on the smooth platinum anode, *viz.* evolution of oxygen (partly ozonized) and formation of peroxodisulphate ions. The two processes are differently affected by increasing the relative concentration of the positively acting cations, as the rate of oxygen evolution decreases, while the rate of peroxodisulphate formation rises. For a quantitative explanation of this effect, the composition of the electric double layer at the existing reaction conditions must be recognized in sufficient detail. Although some progress has been made recently, our knowledge concerning the region of high anodic potentials must be regarded as insufficient, particularly in view of the high number of simultaneously operating factors.

Radioisotope investigations have evidenced that in the region of high anodic potentials, both anions or anion-radicals and cations are adsorbed to a considerable extent^{22,23}. It is interesting that up to approximately 2.6 V the potential regions of adsorption maxima of the cations and the anions alternate. For the region of still higher potentials, which is the most interesting from the point of view of the maximum peroxodisulphate yields, data concerning the adsorption of cations are so far lacking; the existence of this adsorption has been, however, corroborated by double layer capacity measurements¹⁷.

The simultaneous adsorption of cations and anions on the oxidized platinum anode has been explained^{10,11} in terms of formation of a first layer of strongly sorbed anions or anion-radicals, which to an extent displace the sorbed molecules of water. This sorbed anion layer is supposed not to take part in the subsequent process of anodic formation of peroxodisulphates. The cations, occurring in the solution in hydrated state, are sorbed secondarily on this first anion layer and are assumed to enhance the ψ_1 potential at the electrode. This adsorption enables formation of ionic bridges between additional anions, thereby accelerating the anodic discharge of the anions with the formation of peroxodisulphates. This effect is in fact analogous to the effect of cations on the rate of homogeneous chemical reaction between peroxodisulphates and other anions in solution^{24,25}.

According to Frumkin¹⁴, the adsorbed cations slow down the oxygen evolution by strengthening the bond of surface chemisorbed oxygen films, which are intermediate product of oxygen evolution. Smit and Hoogland¹¹ do not agree with this view and offer another explanation; they also pointed at the possibility of affecting the activity of water in the by-electrode layer by the cations present, whose hydration degree decreases with increasing atomic radius.

In our opinion, the fact that positively acting cations affect the peroxodisulphate formation and the simultaneous oxygen evolution in opposite directions, rests in their secondary adsorption made possible by the primary adsorption of anions or anion-radicals on the platinum anode coated with oxide films. The cations probably do not turn completely dehydrated during this adsorption. The resulting effect depends on their effective ionic radii, including also the molecules of hydration water, and on the charge density, which is inversely proportional to the cation radius.

The increase in the rate of peroxodisulphate formation brought about by the low-hydrated cations (Cs^+ , Rb^+ , K^+ , NH_4^+) with lower ionic radii can be explained so that owing to their secondary adsorption and ionic bridge formation they are able to draw another layer of anions to a closer vicinity of the platinum anode and thus to accelerate their discharge. At the same time, because of their lower hydration these cations introduce a lower number of water molecules into the outer Helmholtz layer and thereby make the evolution of gaseous oxygen more difficult. According to this concept, a dominant part of gaseous oxygen is really formed on account of discharge of water molecules, and the participation of anion discharge in the oxygen evolution at high anodic potentials is rather low, as has been also confirmed by analogous measurements by means of ^{18}O in perchloric acid solutions²⁶.

Cations hydrated to a higher degree (*e.g.*, H^+ , Li^+ , Mg^{2+} , Cd^{2+} , Zn^{2+} , Al^{3+}), being rather bulky, are adsorbed on the oxidized surface of the anode to a lesser extent, in spite of the higher total charge in the case of the di- and trivalent ions; thus their ability to accelerate the anion discharge *via* the ionic bridges is reduced. On the other hand, they introduce a considerably higher amount of water into the by-electrode layer owing to their high hydration, whereby the oxygen evolution is favoured. Inasmuch as these cations are more hydrated than the H^+ ions, the former behave as negatively acting components with respect to the peroxodisulphate formation. Thus the effect of these negatively acting components, ascribed formerly to their catalytic activity⁵⁻⁷, can be explained in a unified manner.

The above concept is supported by Fig. 5, showing the relation between the maximum current yields of peroxodisulphates in the solutions *I* and *II* and the hydration number, hydration enthalpy or Gibbs energy of the cations concerned²⁷⁻²⁹. In fact, these values pertain to dilute solutions and the actual hydration numbers in the concentrated mixed solutions of interest in the vicinity of the anode polarized to a high potential will obviously be rather different, still some relations can be assumed to be preserved. Really, Fig. 5 demonstrates that the maximum current yields of peroxodisulphates roughly decrease with increasing hydration parameters of the cations involved, especially in the case of alkali metal and ammonium cations. This can be ascribed to the fact that in the case of these cations, whose hydration numbers are appreciably lower than those of the other cations pursued, the first coordination sphere is not completely occupied by water molecules, particularly in more concentrated solutions. As a consequence, even low absolute differences between the hydration

numbers are in this case reflected by the two independent anodic processes to an appreciably higher extent than with the other cations, whose hydration numbers are considerably higher, largely surpassing the coordination numbers of the first co-sphere. Such highly hydrated cations promote particularly the discharge of water molecules with the formation of gaseous oxygen, the current yields of peroxodisulphates are lower than in pure sulphuric acid, their dependence on the hydration number or hydration Gibbs energy, however, is not very marked (Fig. 5). For a quantitative interpretation of the dependences observed, series of additional measurements would be necessary, particularly those related to the adsorption of the various cations on the oxidized surface of the platinum anode and the degree of their hydration in the reaction conditions applied.

The variations in the order of efficiency of positively acting cations with respect to the current yields of peroxodisulphates that were observed on changing the overall current density j_a (Fig. 2) or the anodic potential are reminiscent of the varying effect of alkali metal ions on the oxygen overpotential in sulphuric acid solutions with changing activity of water^{12,16}. Within the concept suggested, this analogy is straightforward, since changes in current density or anodic potential are accompanied by changes in the adsorbed amount of the hydrated cations and thereby in the activity of water in the by-electrode layer, from which gaseous oxygen evolves.

The shift of the partial polarization curves of peroxodisulphate formation accompanying the increasing relative content of positively acting ions (for instance, NH_4^+ , see Fig. 3), regarded as an evidence of the accelerating effect of the cations on the formation of S_2O_8^- ions is, however, at least partly due to the shift of the equilibrium potential of the system in the same direction. In fact, the substitution of a portion of H_2SO_4 by the corresponding amount of $(\text{NH}_4)_2\text{SO}_4$ brings about

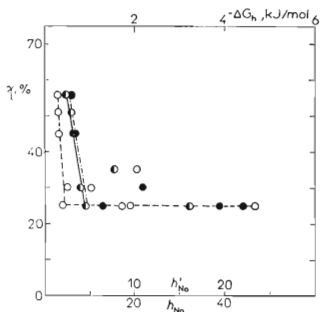


FIG. 5

Dependence of Maximum Current Yields of Peroxodisulphates for Electrolysis of Solutions of $5\text{M-H}_2\text{SO}_4 + 1\text{M}$ or $0.1\text{M-M}_x\text{SO}_4$ on the Hydration Number (h_{No}) or the Hydration Gibbs Energy of the Cation M

○ Hydration Gibbs energy²⁷, ● hydration numbers (h_{No}) from the transference numbers²⁸ (lower scale); ● hydration numbers from the adiabatic compressibilities²⁸ (upper scale). h_{No} = hydration number from adiabatic compressibilities, h'_{No} = hydration number from transference numbers.

an increase in the actual concentration of SO_4^{2-} ions, whose discharge and dimerization results in a considerably faster formation of the $\text{S}_2\text{O}_8^{2-}$ ions than the discharge of the HSO_4^- ions, predominating in sulphuric acid solutions¹⁸.

Assuming that the overall degree of conversion to peroxodisulphate ions is constant, whereby the peroxodisulphate concentration is constant too, and that the activity coefficients of the various ions in the electrolyzed solutions of the same total concentration are also constant, the equation for the equilibrium potential of formation of peroxodisulphates at 25°C (ref.³⁰),

$$E = 2.010 + 0.0295 \log (a_{\text{S}_2\text{O}_8^{2-}}/a_{\text{SO}_4^{2-}}^2), \quad (1)$$

can be rewritten as

$$E = \text{const} - 0.059 \log c_{\text{SO}_4^{2-}}, \quad (2)$$

where the concentration term refers to the actual concentration of sulphate ions in the solution electrolyzed; these values for mixed concentrated solutions of sulphuric acid and ammonium sulphate are so far unknown. Under the simplifying assumption that the actual concentration of the sulphate ions can be equated with the ammonium sulphate concentration, the equilibrium potentials of the systems of initial compositions $2\text{M}-(\text{NH}_4)_2\text{SO}_4 + 4\text{M}-\text{H}_2\text{SO}_4$ and $3\text{M}-(\text{NH}_4)_2\text{SO}_4 + 3\text{M}-\text{H}_2\text{SO}_4$ can be expected to be approximately 18 mV and 28 mV, respectively, more negative than the potential of the system of the initial composition $1\text{M}-(\text{NH}_4)_2\text{SO}_4 + 5\text{M}-\text{H}_2\text{SO}_4$, for the same, very low degree of conversion. The observed differences, however, were as high as 32 to 44 mV and 45 to 65 mV, respectively (the values varied according to the current density applied). Chu Yung-chao¹⁰ has found a shift of approximately 50 mV between the polarization curves pertaining to solutions of $3\text{M}-\text{H}_2\text{SO}_4 + 1\text{M}-(\text{NH}_4)_2\text{SO}_4$ and $2\text{M}-\text{H}_2\text{SO}_4 + 2\text{M}-(\text{NH}_4)_2\text{SO}_4$ for electrolysis temperature 7°C. Thus in all cases the observed shifts of the polarization curves are approximately twice as high as the theoretical values resulting only from the changes in the equilibrium potentials brought about by the changing actual concentration of the more rapidly discharging SO_4^{2-} ions. This gives evidence that the positively acting cations, being adsorbed on the platinum anode, not only enhance the oxygen overpotential, but also really accelerate the anodic discharging of sulphate ions with the formation of peroxodisulphates.

In a sense, the role of Li^+ ions is exceptional, since in the reaction conditions used they relatively raise both the oxygen overpotential and the peroxodisulphate formation rate. The resulting current yields of peroxodisulphates are somewhat lower than in pure sulphuric acid. This is analogous to the anomalous behaviour of Li^+ ions in a number of other systems and reactions, supporting data for a reliable explanation of this effect are, however, lacking.

REFERENCES

1. Machu W.: *Das Wasserstoffperoxyd und die Perverbindungen*, 2nd Ed. Springer, Wien 1951.
2. Schumb W. C., Satterfield C. N., Wentworth R. L.: *Hydrogen Peroxide*. Reinhold, New York 1955.
3. Regner A.: *Technická elektrochemie I. Elektrochemie anorganických látek*, p. 560. Academia, Prague 1967.
4. Elbs K., Schönherr O.: *Z. Elektrochem.* 1, 245 (1895).
5. Müller E., Schellhaas H.: *Z. Elektrochem.* 13, 257 (1907).
6. Essin O., Alfimova E.: *Z. Elektrochem.* 41, 260 (1935).
7. Matsuda R.: *Bull. Chem. Soc. Jap.* 11, 1 (1936).
8. Izgaryshev N. A., Petrova A. A.: *Zh. Fiz. Khim.* 24, 881 (1950).
9. Chu Yung-chao, Mi Tien-yin: *Sci. Rec.* 2, 443 (1958); *Dokl. Akad. Nauk SSSR* 125, 1069 (1959).
10. Chu Yung-chao in the book: *Osnovnye Voprosy Sovremennoi Elektrokhemii* (A. N. Frumkin, Ed.), p. 132. Nauka, Moscow 1973.
11. Smit W., Hoogland J. G.: *Electrochim. Acta* 16, 1, 821, 961 (1971).
12. Erdey-Grúz T., Safarik I.: *Acta Chim. (Budapest)* 13, 159 (1958).
13. Frumkin A. N., Kaganovich R. I., Yakovleva E. V., Sobol V. V.: *Dokl. Akad. Nauk SSSR* 141, 1416 (1961).
14. Frumkin A. N.: *Electrochim. Acta* 5, 265 (1961).
15. Kaganovich R. I., Le Min-lap: *Zh. Fiz. Khim.* 38, 901 (1964).
16. Erdey-Grúz T., Szetey E., Horányi G.: *J. Electroanal. Chem. Interfacial Electrochem.* 65, 177 (1975).
17. Yakovleva A. A., Bairamov R. K.: *Elektrokhemiya* 12, 112 (1976).
18. Balej J., Kadeřávek M.: *This Journal* 44, 1510 (1979).
19. Balej J., Thumová M.: *This Journal* 39, 3409 (1974).
20. Vondrák J., Špalek O.: *Chem. Listy* 64, 609 (1970).
21. Balej J., Regner A.: *This Journal* 30, 1954 (1965).
22. Pospelova N. V., Rakov A. A., Veselovskii V. I.: *Elektrokhemiya* 6, 57, 722 (1970).
23. Naumov V. P., Kazarinov V. E., Tyurin Yu. M.: *Elektrokhemiya* 1973, 9.
24. Karshaw M. R., Prue J. E.: *Trans. Faraday Soc.* 63, 1198 (1967).
25. Chlebek R. W., Lister M. W.: *Can. J. Chem.* 44, 437 (1966); 45, 2411 (1967); 59, 2943 (1971).
26. Kasatkin E. V., Rozental K. I., Veselovskii V. I.: *Elektrokhemiya* 4, 1402 (1968).
27. Friedman H. L., Krishnan C. V., in the book: *Water-A Comprehensive Treatise*, (F. Franks, Ed.). Vol. 3, p. 55. Plenum Press, New York 1973.
28. Burgess J.: *Metal Ions in Solution*. Ellis Horwood, Chichester 1978.
29. Dobos D.: *Electrochemical Data*, p. 101. Elsevier, Amsterdam 1975.
30. Pourbaix M.: *Atlas d'Equilibres Electrochimiques à 25°C*, p. 248. Gauthier-Villars, Paris 1963.

Translated by P. Adámek.